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To cite this article: E A Mikhnevich *et al* 2019 *J. Phys.: Conf. Ser.* **1389** 012059

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Influence of uniform magnetic field on elastic modulus in polyacrylamide ferrogels with embedded nickel nanoparticles

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Abstract. Polyacrylamide ferrogels with embedded nickel magnetic nanoparticles were synthesized by radical polymerization in water. The elastic modulus of ferrogels was measured under unidirectional compression in a uniform magnetic field with a strength of 0, 165, 220 and 275 Oe. With an increase in the content of nickel particles in ferrogel from 0 to 5.3% by weight, the elastic modulus in zero magnetic field increased by 60%. The application of magnetic field parallel to the direction of compression resulted in the increase of modulus, and if the field was applied perpendicular to the compression, the modulus tends to decrease. Such trends are in good agreement with the features of magnetostriction of a non-compressible uniformly magnetized sphere in a constant magnetic field.

1. Introduction

One of the challenging tasks of today's material science is the growing demand for “smart” materials, which term essentially means that a material can mechanically respond to certain external stimuli. More specifically it relates to volume changes, shape distortion, force generation etc. under the controlled variation of external parameters. For instance, such variations may be of thermodynamic, chemical, electrical, and magnetic origin [1,2]. The promising areas for the application of “smart” materials are those associated with health care, biomedicine, and bioengineering. Among other types of the external stimuli, the magnetic field has an advantage as it can be applied distantly without invasion into a living organism. Therefore, much attention is now paid to the development of “smart” magnetic materials for actuators, sensors, drug delivery, MRI and hyperthermia agents due to the prospect of their contactless deformation under the influence of a magnetic field, which opens up wide possibilities for their application [3-5].

Polymeric magnetic materials are extensively studied with this respect as the nature of a polymer provides large elastic deformation in response to the applied magnetic field. Such materials include ferrogels. Ferrogel is a composite consisting of two sub-systems: an elastic polymeric network swollen in liquid and magnetic particles immobilized in it [6-8]. Beginning with the first works of Zrinyi et al. [6-11], much effort was focused on the mechanical deformation and magnetostriction of ferrogels in applied magnetic field [12-21], including theoretical studies [22,23] and computer modelling [24-28].

It was shown that the mechanical response of ferrogel is not universal, but it depends on a variety of the internal parameters, such as chemical nature of the polymeric network, volume interaction with the liquid, networking density, the nature of magnetic filler, its content in ferrogel, mean size of



magnetic particles and their size distribution, particle alignment in ferrogel structure. The most extended study was performed by Zrinyi et al. [6,7,10,11] at magnetic silicone elastomers filled with micron sized carbonyl iron or magnetite. The elastic modulus of these magnetoelasts was studied both in the uniform and non-uniform magnetic fields. The influence of the content of magnetic particles and their alignment on the modulus had been systematically studied at different combinations of the orientation of magnetic field and deformation. Meanwhile, the studies on the elastic modulus of water-based synthetic ferrogels are very limited [10, 24-28].

The objective of the present work was to test the influence of the uniform magnetic field on the elastic modulus of polyacryamide ferrogels with embedded nickel magnetic nanoparticles under uniaxial compression load. The dependence of the nanoparticle content, the strength, and the orientation of the applied magnetic field on the elastic modulus had been studied.

2. Experimental part

2.1. Synthesis and characterization of MNPs

Nickel magnetic nanoparticles (Ni MNPs) were synthesized by the electrical explosion of wire (EEW) method [29]. The essence of EEW is the evaporation of a metal wire by a high-voltage electric discharge in an inert atmosphere of argon and the subsequent condensation of metal vapours into spherical nanoparticles. The details of the synthetic procedure can be found in our previous reports [29-31].

Figure 1 shows transmission electron microscopy (TEM) image (JEOL JEM2100) of Ni MNPs. MNPs are spherical in shape and non-agglomerated.

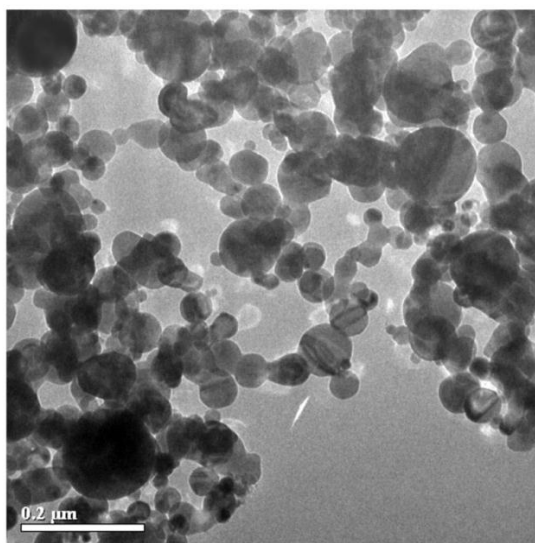


Figure 1. TEM micrograph of Ni MNPs (JEOL JEM2100).

Particle size distribution of Ni MNPs, evaluated by the graphical analysis of 2190 images was lognormal with median 55.2 nm and logarithmic dispersion 0.381. The number averaged particle diameter calculated from PSD was 57.9 nm, and the weight averaged diameter was 84.6 nm. The specific surface area of MNPs of 12.6 m²/g was determined by the low-temperature sorption of nitrogen vapors technique using an automatic sorption unit “Micromeritics TriStar 3000”.

The phase composition of the magnetic filler was characterized by X-ray diffraction technique (XRD) using the BrukerD8 Discover diffractometer. According to X-ray powder diffraction data, the Ni nanopowder contains a 100% α -Ni phase with a cubic face-centered lattice (figure 2).

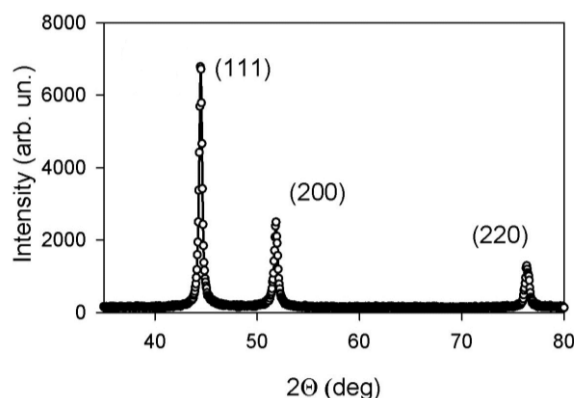


Figure 2. XRD diffractogram of Ni MNPs (Bruker D8 Discover). Miller indexes are shown for each bright peak.

Magnetic properties of Ni MNPs were measured at room temperature by a vibromagnetometer (VSM). The value of saturation magnetization was as high as $M_s = 51.1$ emu/g, the remanent magnetization $M_r = 17.7$ emu/g, and the coercivity $H_c = 260$ Oe. These values characterize Ni as relatively soft magnetic material (figure 3) with saturation magnetization just slightly lower the M_s value corresponding to the bulk Ni. The observed M_s decay is connected with small size of MNPs and contribution of scaling effects as well as it can be explained by the presence of very thin oxide passivation layer on the MNPs surface.

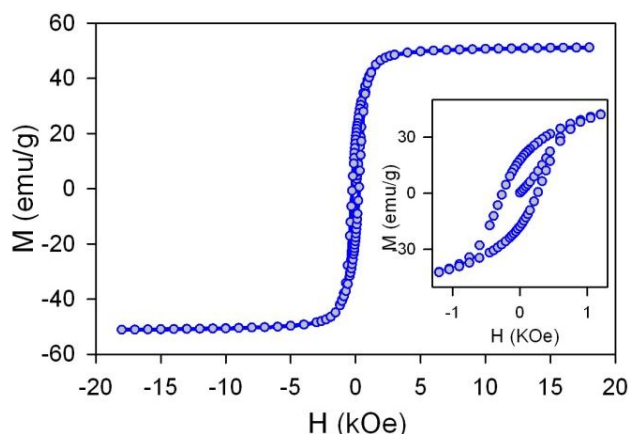


Figure 3. Magnetic hysteresis loop and primary magnetization curve of Ni MNPs measured at room temperature. Inset – enlarged view of low field range

2.2. Synthesis and characterization of ferrogels

Ferrogels with embedded Ni MNPs were synthesized by radical polymerization in water. The monomer - acrylamide (AAm) (Panreac Quimica SA) was used at 2.7 M concentration. Methylene diacrylamide (MDAA) (MERCK) served as a crosslinking agent at a molar ratio to the monomer 1:100. Ammonium persulphate (PSA) was used as the initiator of the polymerization reaction, and the catalyst for the polymerization reaction was N, N, N', N'-tetraethylmethylene-1,2-diamine (TEMED). Ni MNPs were added to the reaction mixture in weighted portions of a water-based 20% slurry, stabilised with Dispex A40 dispersant (R.T. Vanderbilt). The slurry was homogenized in ultrasound bath for 20 min. Linear polyacrilamide (PAAm) ($MW = 2 \cdot 10^5$) at 3.3% concentration by weight was added to the reaction mixture as a thickener to prevent precipitation of Ni MNPs. Polymerization was performed at room temperature for 5 min until gelation occurred and the reaction mixture lost its fluidity and then 60 min at 80°C to accomplish the reaction. Three ferrogels with increasing content of Ni MNPs and the blank gel without MNPs were synthesized.

The obtained ferrogels were washed in distilled water for two weeks with daily water renewal to remove catalyst, salts, dispersant, and linear oligomers. The equilibrium swelling degree (maximum

water uptake) was determined as the ratio of water content in the gel to the weight of the dry gel by weighting the swollen specimen of a gel and the residue after drying at 70°C in vacuum. The weight content of Ni MNPs in swollen ferrogels was 0.0, 1.8, 3.6 and 5.3% by weight (TG/DSC analysis, NETZSCH STA409). Further on they are denoted as FG0, FG1, FG2, FG3. The photograph of ferrogel and corresponding PAAm hydrogel is presented in figure 4.



Figure 4. Photographs of PAAm hydrogel (left) and PAAm ferrogel (right).

2.3. Mechanical measurements

The elastic modulus of ferrogels was measured on cylindrical samples in a compression mode using a laboratory setup with optical recording of deformation (figure 5, figure 6).



Figure 5. The laboratory setup for the measurement of the modulus of elasticity: (1) - support for load, (2) – water-cooled Helmholtz coils, (3) – glass cylinder with a forcer, (4) – power source with ammeter, (5) – optical recording camera.

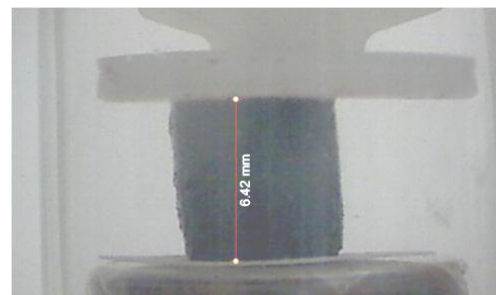


Figure 6. Sample of ferrogel placed in the equipment.

The cylindrical sample was gradually loaded by placing on the upper base of the forcer 1 load from 0 to 100 g. After each load, a sample was photographed, and then the photographs were processed using the MicroCapture computer program.

The measurements in the external magnetic field were made using a water-cooled Helmholtz coils connected in series to a power source. The coils were separated by 4.5 cm gap and were placed either vertically or horizontally. The power source operated in current control mode up to 5 A of the direct current intensity. Mechanical measurements were performed at magnetic field of 0, 165, 220 and 275 Oe. The direction of compression was always vertical and the direction of the field was either vertical (parallel to the compression) or horizontal (perpendicular to the compression) depending on the orientation of Helmholtz coils.

3. Results and discussion

Typical deformation plot for the compression of ferrogel a ferrogel sample without application of magnetic field is given in figure 7. In the range of compression deformation from 0 to 10%, the experimental data are fitted well by linear function $\sigma = 103 \cdot \varepsilon$ (σ – stress ε – relative deformation), which made it possible to calculate the elastic modulus of the ferrogel as the slope of the plot.

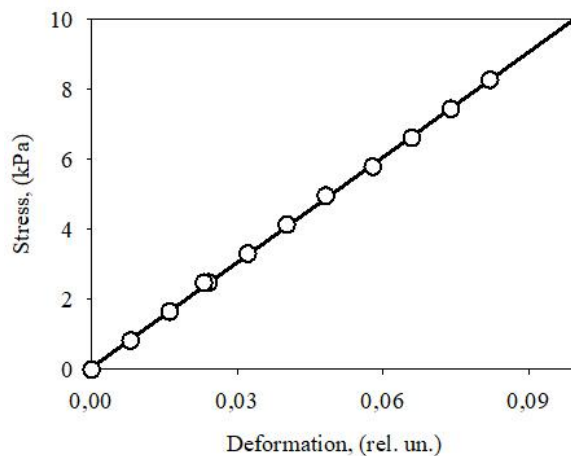


Figure 7. Stress-deformation plot for FG2 ferrogel in zero magnetic field

The calculated values of elastic modulus (G) for ferrogels under study are given in Table 1 together with their swelling degree (Q) and apparent networking density (N). Weight and volume fraction of Ni MNPs in gels are denoted as ω and φ .

Table 1. Swelling degree and modulus of ferrogels.

Gel	ω (%)	φ (%)	G (kPa)	Q	N
FG0	0	0	66	7.4	76
FG1	1.80	0.21	78	6.6	56
FG2	3.64	0.42	95	6.1	44
FG3	5.30	0.62	103	5.9	41

The elastic modulus of composite gel depends on the volume fraction of embedded solid particles according to the Einstein–Smallwood equation:

$$G = G_0(1 + k_E \varphi) \quad (1)$$

where G_0 denotes the modulus of gel without particles and k_E is the Einstein–Smallwood parameter. For noninteracting spherical particles $k_E = 2.5$. Equation (1) describes the reinforcement effect due to

the filler–polymer interaction. Figure 8 presents the dependence of elastic modulus on the volume fraction of Ni MNPs in ferrogel.

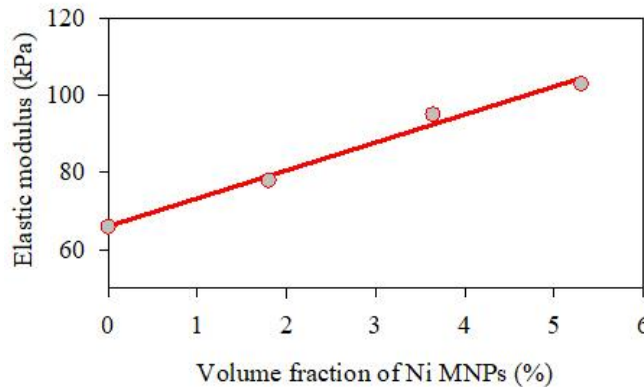


Figure 8. Dependence of the elastic modulus of ferrogels on Ni MNPs content

The values of elastic modulus fitted well the linear dependence $G=66.3+6130*\varphi$, which made it possible to calculate the Einstein–Smallwood parameter k_E (Equation 1). It was found that $k_E=92$, which means strong interaction among Ni particles in ferrogel. Most likely it is the result of strong binding of Ni MNPs to polymeric matrix of ferrogel. It can be seen from Table 1 that the swelling degree of ferrogel (Q) diminishes with the increase of Ni MNPs content. At given chemical composition of a gel Q is a function of a networking density and it decreases if the network becomes more dense. Here it is worth mentioning that Q values given in Table 1 are related solely to the polymeric matrix of ferrogel with the exclusion of non-swelling solid Ni MNPs.

The density of a gel network is characterized by an average number of monomeric units in linear polymeric sub-chains connecting neighbor cross-links. In principle, this value is pre-determined by the monomer-to-cross-linking agent molar ratio in the reaction mixture. However, in reality it can strongly deviate from that. Moreover, linear PAAm was added to the reaction mixture as a thickener, and it can affect the apparent length of linear sub-chains.

The average number of monomeric units (N) in linear sub-chains can be evaluated according to the equation [32]:

$$N = \left(Q \varphi_0^{\frac{1}{4}} \right)^{\frac{8}{3}} \quad (2)$$

where φ_0 stands for the volume fraction of polymer in the reaction mixture after polymerization being accomplished. Calculated values of N for ferrogels based on Q and φ_0 are given in Table 1. It can be clearly seen that N substantially diminishes with the increase of Ni MNPs content. It means that extra cross-links appear in the gel network owing to Ni MNPs. It might be the result of strong adsorption of PAAm sub-chains onto the surface of Ni MNPs. Thus, the solid particles become incorporated in the network and make it mechanically stiffer even at MNPs volume fraction below 1% (Table 1). Consequently the Einstein–Smallwood parameter k_E becomes very large.

The measurements of elastic modulus of ferrogels in the applied external magnetic field were performed in the parallel and perpendicular direction with respect to the direction of compression. It was found that only ferrogel FG3 with the highest Ni MNPs content was mechanically sensitive to the field. Apparently, the content of magnetic particles in FG1 and FG2 was too low to get any change in modulus in magnetic field.

Figure 9 presents the dependence of the elastic modulus of FG2 sample on the magnetic field intensity. At the intensity of magnetic field below 165 Oe no influence of magnetic field on the elastic modulus of ferrogel FG3 was observed. At any orientation of Helmholtz coils the value of the elastic modulus within experimental error was the same as in zero field. Measurable effect appeared at field

strength of 220 and 275 Oe. It was found out that if the magnetic field was applied along the direction of compression, the values of the elastic modulus of the ferrogel increased, and if the field was applied perpendicular to the direction of compression, they decreased. At maximum the elastic modulus changed by 10%.

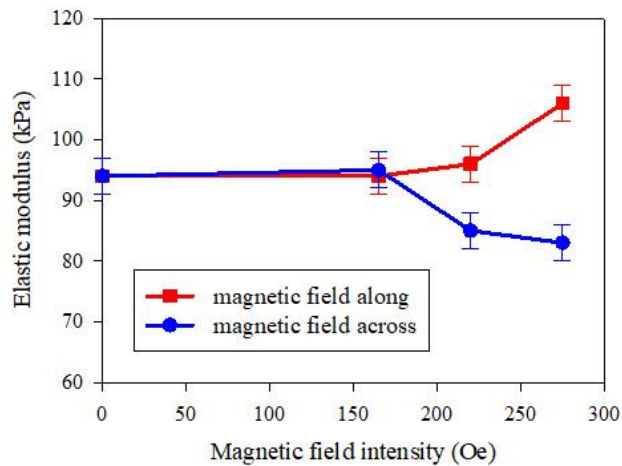


Figure 9. Field dependence of the elastic modulus of FG2 sample.

In general, field dependence of the elastic modulus of ferrogels has the same origin as their magnetostriction. Now it is accepted that the observed magnetostriction of a ferrogel is a balance of two factors. One is the macroscopic demagnetizing effect, based on a balance between magnetic energy and surface energy, which corresponds to the elongation of the sphere along the magnetic field lines and its contraction across the field lines [11]. The other is the structural magnetostriction that stems from the re-grouping of the filler particles at the mesoscopic scale under the action of field-induced interparticle forces [33]. The mechanical stresses (or deformations) due to those two factors depend on the details of particles arrangement at mesoscopic scale and might either sum up or counteract. In the case of ferrogels with Ni nanoparticles studied in present work the macroscopic demagnetizing effect evidently dominates over the mesoscopic structure one, and it results in the increase of the modulus along the field and its diminishing across the field. This result is also supported by computer simulations [23-25] for ferrogels with an isotropic interaction between the polymeric matrix and the magnetic particles. This interaction in the case of ferrogels under study can be caused by van derWaals forces among PAAm sub-chains in the gel network and the surface of Ni NMPs. As it was shown in ref [23-25] in such an architecture of ferrogels the application of magnetic field resulted in the elongation parallel to the field and in the shrinkage in transverse direction.

4. Conclusions

Elastic modulus of polyacrylamide ferrogels with embedded Ni magnetic nanoparticles was measured under unidirectional contraction in a magnetic field with intensity up to 275 Oe. In a zero field the elastic modulus showed up strong dependence on Ni MNPs content. At relatively low volume fraction of MNPs (below 1%) the modulus increased by almost 60%, which indicated strong binding of MNPs to polymeric matrix. The application of magnetic field along the direction of compression increased the elastic modulus, and the application of the field perpendicular the direction of compression decreased it.

Acknowledgments

The study was performed under the financial support of Russian Science Foundation grant 18-19-00090.

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